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THE EFFECT OF NUCLEATORS ON THE QUALITY OF THE SURFACE OF GLASS-CERAMIC DENTURE COATINGS

E. A. Kulinich,¹ T. A. Khabas,¹ and V. I. Vereshchagin¹

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The effect of nucleator additives on the surface relief and the degree of crystallization of material intended for the dentine and enamel layers of artificial denture is considered. It is established that hydroxyapatite additive is optimal for producing the required relief in the prime and dentine layers.

In making metal-ceramic dentures their surface roughness is in fact disregarded and the main attention is paid to the porosity of finished materials. However, the quality of surface is one of the most essential factors ensuring high service parameters of artificial teeth. For normal service of the denture it should have a smooth vitrified surface. The presence of microheterogeneities and roughnesses on the surface of ceramics can result in a premature wear of the patient's own teeth. Furthermore, crowns with such defects have unsatisfactory appearance and get prematurely destroyed by body fluids and tissues. A rough relief creates favorable conditions for life activity of acid-producing bacteria that contribute to the erosion of ceramics and natural enamel. Note that this statement holds only for the surface layers of the multilayer ceramic composite (dentine, enamel). Roughness in the prime layer is desirable, since a microheterogeneous relief is needed to increase the adhesion between the prime coat and the other layers.

The roughness of surface in engineering is estimated based on the unevenness of the profile obtained by intersecting the real surface with a plane. The averaged profile line is taken as the reference base to estimate the deviation of the profile. Standard GOST 27964–88 (extended to all types of materials) takes into account the roughness of surface regardless of its production method. For quantitative estimate and standardizing of the surface roughness the main parameters are R_a and R_z representing the average height of irregularities of the profile (R_a denotes all irregularities and R_z denotes the maximum irregularities). Thus, the higher the surface roughness, the larger are numerical values of R_a and R_z [1, 2].

In this study the surface relief of samples was analyzed using a "Micromesure 3D non contact Profilometry" instrument (France). The scanning beam diameter is 2 μm , the

scanning surface area is 0.25 cm^2 . The results of analysis are displayed as a 3-D image of the scanned surface and the surface profile (roughness) along the scanning beam track. Using ready feldspar glass frits (USSR Inventor's Certif. No. 2233650) [3, 4] we prepared mixtures with additives of compounds initiating crystallization in an amount of 0.10, 0.25, 0.40, and 0.50 wt.%. These additives were TiO_2 , ZrO_2 , Al_2O_3 , and hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, respectively.

To clarify the effect of nucleator additives on the material surface relief, crystallizing additives were introduced in two ready feldspar glass frits arbitrarily termed "dentine" and "enamel" that were intended for the production of the dentine and enamel layers of artificial denture. The frits were melted in air at a temperature of 1200°C. The ready mixtures were molded as cylinders of diameter 10 and height 5 mm, the molding pressure was 50 MPa. The samples based on dentine and enamel were fired in air at the temperatures of 850 and 750°C, respectively. After firing, the untreated surface of the samples was scanned.

In general the following regularity is observed for all samples: with an increasing content of the crystallization-initiating oxide the parameter R_a grows (Fig. 1).

It is established that virtually in all cases a clearly defined relief corresponds to a more crystallized material due to the growth and enlargement of leucite crystals on its surface. The largest crystals are registered on the surface and in the bulk of the samples with TiO_2 additive. A more uniform increase in roughness and (presumably) crystallization capacity is registered in hydroxyapatite and Al_2O_3 . Samples based on an amorphous enamel with a slight (not more than 1%) quantity of nucleator have a smooth surface with a nearly unexpressed relief.

It should be noted that surface roughness grows not only due to crystallization occurring inside the volume and on the surface of samples, but also due to their increasing porosity. Numerous fine pores are visible on the surface of samples

¹ Tomsk Polytechnic University, Tomsk, Russia.

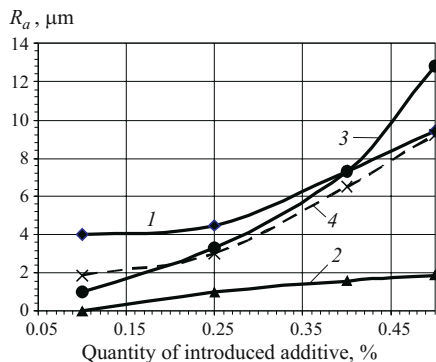


Fig. 1. Dependence of surface roughness of dentine on the quantity of nucleator additive: 1, 2, 3, and 4) Al_2O_3 , ZrO_2 , TiO_2 , and hydroxyapatite additives, respectively.

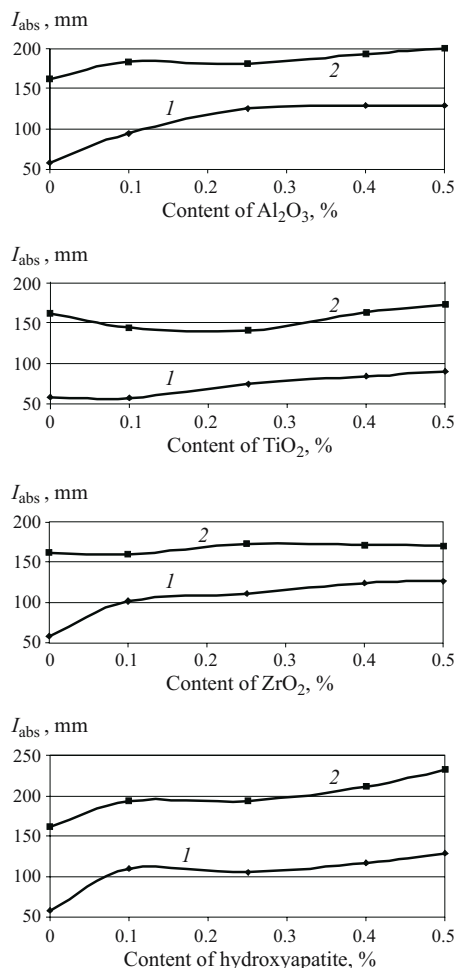


Fig. 2. Intensity of x-ray reflections of leucite ($d = 0.325$ nm) versus the quantity of nucleator additive: 1) enamel; 2) dentin.

employing a microscope and under subsequent scanning of the sample surface these pores produce an erroneous image of the profile, since the pore size exceeds significantly the size of emerging crystals. According to GOST R 51735–2001, the admissible number of pores is not more than 16 pores of

a diameter over $30 \mu\text{m}$ per 1 mm^2 of the surface area. Precisely for this reason (with the aim of decreasing porosity) ceramic layers on a metal substrate need to be fired in vacuum and not under atmospheric pressure.

The x-ray phase analysis of the sample established that all obtained systems are polymineral. Their main crystalline phase is leucite, but the initial phases (microcline, orthoclase) and potassium aluminosilicate KAlSi_3O_8 are present as well. Dentine samples are generally more crystallized than enamel samples. Upon introducing nucleator additives, the intensity of the x-ray reflection of leucite ($d = 0.325$ nm) mainly grows in proportion to the amount of additive introduced (Fig. 2).

Hydroxyapatite and Al_2O_3 additives have the maximum effect on crystallization: the diffraction patterns of samples containing these additives exhibit the maximal increase in the x-ray reflection of leucite. Enamel-based compositions are more susceptible to the effect of crystallization-initiating additives than dentine-based compositions.

The measurements of the CLTE of samples bearing different quantities of nucleator additives indicate that as the content of additive grows, the CLTE of amorphous enamel composition mainly increases and the CLTE of dentine composition slightly decreases. The introduction of hydroxyapatite into amorphous compositions increases their expansion under heating. Apparently, hydroxyapatite becomes partly dissolved in glass at the temperature of frit melting, therefore, the increased calcium content facilitates an increase in the CLTE.

As for microhardness, the samples with hydroxyapatite additives introduces as crystallization initiators are the closest to natural teeth (the microhardness of such samples is equal to 3893 – 4279 MPa, the microhardness of natural dental enamel is 3240 – 3430 MPa). The chemical resistance of all considered samples satisfies the requirements of GOST R 51735–2001.

Next, we estimated the surface relief of all ceramic layers of the coating (prime layer, dentine, and enamel) consecutively deposited on a cobalt-chromium substrate (Fig. 3). The roughest is the prime coat. This facilitates a better adhesion of the subsequent ceramic layers to the metallic structural base.

The roughness of the main (dentine) layer is less perceptible and visually its surface appears smooth enough. A slight roughness due to the presence of a small quantity of open micropores on the dentine surface improves the fixation of the final (enamel) coat. The surface of the enamel coat is even, lustrous, and vitrified.

Thus, the relief of each deposited coat in the proposed coating corresponds to its destination: the rough prime and dentine coats ensure good adhesion of the layers, whereas the smooth enamel layer provides good aesthetic and mechanical properties to the finished coating.

The following regularity is observed in the investigated additive series, i.e., hydroxyapatite – Al_2O_3 – ZrO_2 – TiO_2 :

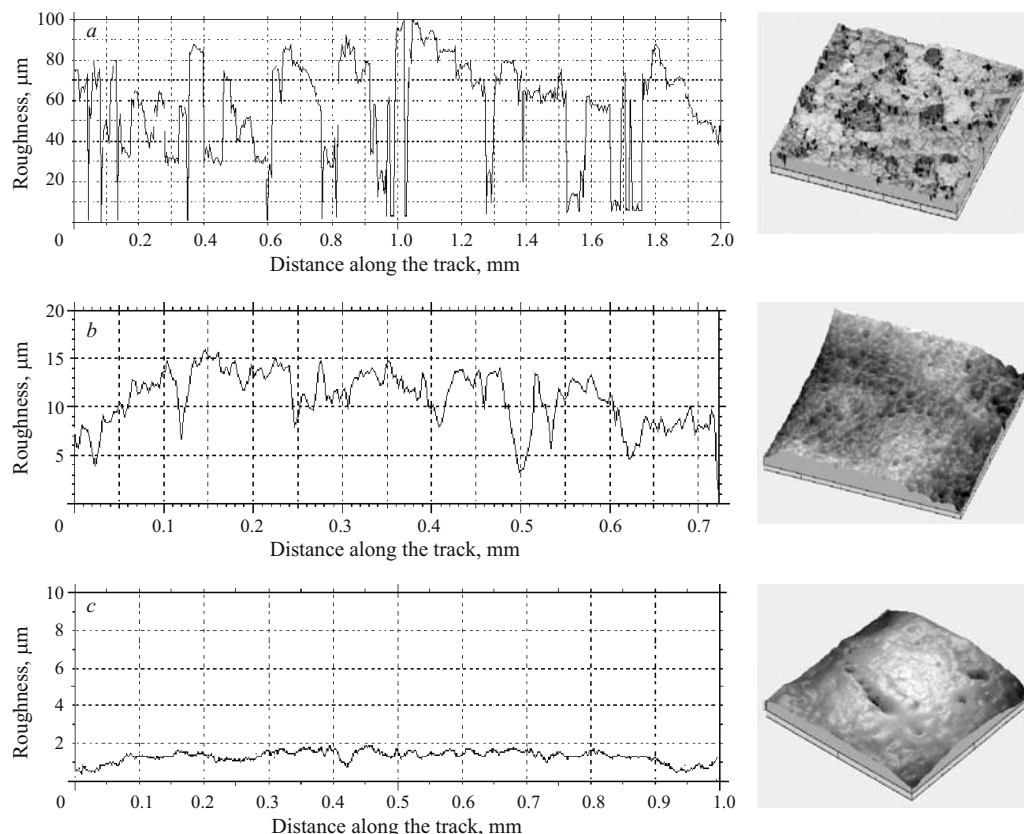


Fig. 3. Surface relief of finished coatings after consecutive deposition of layers and their firing at prescribed temperatures: *a*) prime coat, $R_a = 19.7$ nm, $R_z = 100$ nm; *b*) dentine layer, $R_a = 1.49$ nm, $R_z = 12.4$ nm; *c*) enamel layer, $R_a = 0.53$ nm, $R_z = 3.17$ nm.

the quantity of leucite in the finished frit decreases from hydroxyapatite to TiO_2 , i.e., in this series hydroxyapatite is the most effective nucleator. At the same time, the analysis of the surface relief of samples with the specified additives established that TiO_2 provides the maximum roughness, i.e., a substantial growth of glass-ceramic crystals.

In making glass ceramic materials for medical purposes, it is preferable to use hydroxyapatite as the nucleator additive and inadvisable to use TiO_2 . Enamel-based frits are more susceptible to the effect of nucleator additives.

Ceramic coatings with hydroxyapatite additives are the closest to natural teeth in their mechanical parameters.

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